# UNITED STATES PATENT APPLICATION

 $\mathbf{OF}$ 

SOO-SIK YOON
GEUN-YOUNG YEOM
NAE-EUNG LEE
KI-JOON KIM
CHANG-HYUN OH
AND
JI-HWANG KIM

**FOR** 

CLEANING METHOD OF APPARATUS FOR MANUFACTURING
SEMICONDUCTOR DEVICE

[0001] The present invention claims the benefit of Korean Patent Application No. 2003-05789, filed in Korea on January 29, 2003, which is hereby incorporated by reference.

## **BACKGROUND OF THE INVENTION**

## Field of the Invention

[0002] The present invention relates to a cleaning method of an apparatus for manufacturing a semiconductor device, and more particularly, to a cleaning method of an apparatus for depositing thin films.

## Discussion of the Related Art

[0003] Thin films of a semiconductor device are formed by various methods including a chemical vapor deposition (CVD) method. After depositing each thin film, a chamber of a deposition apparatus is cleaned so as to remove source gases and residual products remaining on an inner wall of the chamber and in the chamber.

[0004] Perfluorocompound (PFC) gases, such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>8</sub>, and SF<sub>6</sub>, may be used as gases for removing silicon, silicon oxide (SiO<sub>X</sub>) or silicon nitride (SiN<sub>X</sub>) existing in the chamber. However, in the case of cleaning the chamber by using the PFC gases, global warming gases may be exhausted because the PFC gases may have low efficiency and may be recombined in an outlet of the chamber. The global warming gases absorb infrared (IR) rays and cause global warming. Thus, in cleaning the camber for the deposition apparatus, several methods, which use gases substituting the PFC gases or reduce quantity of the global warming gases while using the PFC gases, have been proposed.

[0005] Recently, NF<sub>3</sub> is widely used as a cleaning gas substituting the PFC gases, and NF<sub>3</sub> has a high cleaning rate and discharge extremely small quantities of the global warming

gases. By the way, since NF<sub>3</sub> is formed through complicated processes, NF<sub>3</sub> is short of supply. Therefore, NF<sub>3</sub> is provided at a high price, and raise a manufacturing cost. In addition, when the chamber for the deposition apparatus is cleaned using NF<sub>3</sub>, poisonous fluorine gas (F<sub>2</sub>) may be formed as a residual product. F<sub>2</sub> corrodes the inner surfaces of the chamber during cleaning, and thus the apparatus for manufacturing the semiconductor device may be damaged.

[0006] Other cleaning gases have been suggested, but the cleaning gases have lower cleaning rates as compared with NF<sub>3</sub>.

## **SUMMARY OF THE INVENTION**

[0007] Accordingly, the present invention is directed to a cleaning method of an apparatus for manufacturing a semiconductor device that substantially obviates one or more of problems due to limitations and disadvantages of the related art.

[0008] An advantage of the present invention is to provide a cleaning method of an apparatus for manufacturing a semiconductor device that prevents global warming.

[0009] Another advantage of the present invention is to provide a cleaning method of an apparatus for manufacturing a semiconductor device that reduces global warming gases released after cleaning the apparatus.

[0010] Another advantage of the present invention is to provide a cleaning method of an apparatus for manufacturing a semiconductor device that increases cleaning rates and improves efficiency of processing.

[0011] An advantage of the present invention is to provide a cleaning method of an apparatus for manufacturing a semiconductor device that cleans uniformly the inner side of a chamber of the apparatus.

[0012] Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0013] To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described, a cleaning method of an apparatus for manufacturing a semiconductor device includes providing a first cleaning gas and a second cleaning gas into a chamber, and forming a mixture of the first cleaning gas and the second cleaning gas, wherein the first cleaning gas includes a fluorocarbon gas and an oxygen gas and the second cleaning gas includes nitrogen, activating the mixture of the first cleaning gas and the second cleaning gas by a high frequency power, and exhausting residues cleaned by the activated mixture and remaining gases.

[0014] In another aspect of the present invention, a cleaning method of an apparatus for manufacturing a semiconductor device includes activating a first cleaning gas by a high frequency power, wherein the first cleaning gas includes a fluorocarbon gas and an oxygen gas, activating a second cleaning gas by a high frequency power, wherein the second cleaning gas includes nitrogen, mixing the activated first cleaning gas and the activated second cleaning gas, thereby forming a mixture of the first cleaning gas and the second cleaning gas, and exhausting residues cleaned by the mixture and remaining gases.

[0015] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

## **BRIEF DESCRIPTION OF THE DRAWING**

[0016] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

[0017] In the drawings:

[0018] FIG. 1 is a schematic view showing an apparatus for manufacturing a semiconductor device used in the cleaning method according to a first embodiment of the present invention; and

[0019] FIG. 2 is a schematic view showing an apparatus for manufacturing a semiconductor device used in the cleaning method according to a fourth embodiment of the present invention.

## DETAILED DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

[0020] Reference will now be made in detail to the illustrated embodiments of the present invention, the examples of which are illustrated in the accompanying drawings.

[0021] In the present invention, a first cleaning gas and a second gas are used to clean a chamber for a deposition apparatus. The first cleaning gas includes a fluorocarbon gas and an oxygen gas and the second cleaning gas includes nitrogen. The second cleaning gas is supplied at a regular rate to the first cleaning gas.

[0022] The fluorocarbon gas, beneficially, may be one of  $C_3F_8$ ,  $C_4F_8$  and  $C_4F_8O$ . The fluorocarbon gas is activated to F radical by plasma, and is exhausted by reacting silicon in silicon, silicon nitride or silicon oxide remaining in the chamber and forming  $SiF_4$ . Therefore, the cleaning process is performed.

[0023] The oxygen gas diffuses the fluorocarbon gas and the second cleaning gas including nitrogen. Additionally, the oxygen gas prevents the fluorocarbon gas from being a polymer such as  $(CF_2)_n$  and improves a cleaning rate by oxidizing residues in the chamber.

[0024] The fluorocarbon gas and the oxygen gas are supplied into the chamber or into a plasma generating system, which may be independently disposed outside the chamber, thereby forming the first cleaning gas of the present invention. The cleaning rate may increase with the addition of the fluorocarbon gas and the oxygen gas, and global warming gases released during the cleaning process are also increased. Thus, The fluorocarbon gas and the oxygen gas should be provided at an appropriate rate.

[0025] The oxygen gas should be more than the fluorocarbon gas, and beneficially, the flow rate of the fluorocarbon gas to the oxygen gas may be 0.1 to 0.5. If the fluorocarbon gas is supplied less than the above flow rate, it is hard to obtain expected cleaning effect. If the fluorocarbon gas is supplied more than the above flow rate, a proper cleaning efficiency to the increased flow cannot be achieved because the remaining time in the chamber decreases due to the increased flow.

[0026] On the other hand, as stated above, the cleaning gas of the present invention includes the second cleaning gas having nitrogen. The second cleaning gas is supplied to have a flow rate of about 0. 01 to 0.5 to the first cleaning gas. If the second cleaning gas is supplied less than the above flow rate, the cleaning effect cannot be expected, and if the

second cleaning gas is supplied more than the above flow rate, the cleaning rate and the decrease of the global warming effect are not effective for the increased flow rate.

[0027] The second cleaning gas may be selected from one of  $N_2$ , NO and  $N_2O$ . The second cleaning gas is activated to NO or NO radical by plasma, and removes nitrogen or oxygen on a surface of a film remaining in the chamber as shown in the following reaction formulas (1) to (4), thereby accelerating reaction between silicon on the surface of the film, where nitrogen or oxygen is removed, and F radical, which is formed by dissociating the fluorocarbon gas.

[0028] NO + Si-N(s) 
$$\rightarrow$$
 Si(s) + N<sub>2</sub>O (1)

$$[0029] N + O \rightarrow NO$$
 (2)

[0030] NO + Si-O(s) 
$$\rightarrow$$
 Si(s) + NO<sub>2</sub> (3)

[0031] 
$$NO_2 + O \rightarrow NO + O_2$$
 (4)

[0032] In addition, the oxygen gas in the first cleaning gas and the second cleaning gas lower global warming potentials of gases emitted during the cleaning process. The fluorocarbon gas of the present invention may be recombined during the cleaning process, and forms CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>8</sub>, COF<sub>2</sub>, SiF<sub>4</sub>, HF, and so on.

[0033] Among the above gases including fluorine, carbon tetrafluoride (CF<sub>4</sub>), which has a high global warming potential, reacts O radical dissociated from the oxygen gas by plasma, and is changed to a gas having a low global warming potential, such as CO<sub>X</sub> or COF<sub>X</sub>. Or CF<sub>4</sub> reacts N radical dissociated from the second cleaning gas, and is changed to CN or NF<sub>X</sub> having a low global warming potential. Therefore, the cleaning gas of the present invention reduces the global warming effect due to PFC gases formed during the cleaning process of the chamber.

[0034] Destruction of feed gas and the effect of emitted gases on global warming are quantified as destructive removal efficiencies (DREs) and million metric tons of carbon equivalents (MMTCEs), respectively. DRE and MMTCE values are calculated by using the following equations (1) and (2), respectively;

[0035] DRE(%) = 
$$[1-C_0/C_i] \times 100$$
, equation (1)

[0036] where  $C_i$  is the gas volumetric concentration before the plasma cleaning and  $C_o$  is the gas volumetric concentration after the plasma cleaning, and

[0037] MMTCE = 
$$\Sigma 12/44 \times \{Q(kg) \times GWP / 10^9\}$$
, equation (2)

[0038] where Q is the total mass of gases (in Kg) released during the cleaning process, and GWP is the global warming potential of each component (integrated over a 100 year time horizon).

[0039] Exemplary embodiments will be explained hereinafter with reference to attached drawings.

#### [0040] First embodiment

[0041] FIG. 1 shows a schematic view of an apparatus for manufacturing a semiconductor device used in the cleaning method according to a first embodiment of the present invention. In the first embodiment of the present invention, a remote plasma generator 70 outside a chamber 10 is used to activate cleaning gases. One part of the remote plasma generator 70 is connected to a radio frequency (RF) power supply 20, and the other part of the remote plasma generator 70 is grounded. A gas inlet (not shown) is connected to the remote plasma generator 70. Plasma formed in the remote plasma generator 70 flows in the chamber 10 through a plasma inlet 31. A substrate holder 16 is disposed in the chamber 10, and an exhaust line 32 is connected to the chamber 10 to exhaust cleaning residues. The

exhaust line 32 is also connected to a booster pump 34 and a dry pump 36, and a control valve 40 is located in the exhaust line 32. The pressure in the chamber 10 can be regulated by the control valve 40. Nitrogen gas (N<sub>2</sub>) is used as a purging gas of the dry pump 36, and a flow rate of N<sub>2</sub> is uniformly maintained during a cleaning process. The remote plasma generator 70 may use a remote inductively couple plasma (ICP) source.

[0042] A cleaning rate of the chamber 10 is measured by a step-profilermeter 50, and a Fourier transform Infrared (FT-IR) spectrometer 60 is equipped at one end of the exhaust line 32 to measure the MMTCE of the PFC gases released during the cleaning process.

[0043] The remote plasma generator 70 uses 13. 56 MHz as a RF power. During the cleaning process, RF power applied to the remote plasma generator 70 is about 500Watts and the pressure in the chamber 10 is about 300mTorr. Silicon nitride (not shown) is used as samples for measuring the cleaning rates of the chamber 10, and the samples are located at the center of the substrate holder 16, at the side wall of the chamber 10, and at the front wall of the chamber 10, respectively.

[0044]  $C_4F_8$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2O$  is used as the second cleaning gas.  $C_4F_8$  of about 20sccm and  $O_2$  of about 140sccm are supplied into the remote plasma generator 70, because the highest cleaning rate for the silicon nitride is obtained at  $C_4F_8(20\text{sccm})/O_2(140\text{sccm})$ . The cleaning rate of  $C_4F_8/O_2$  without the second cleaning gas is about 110 nm/min.

[0045] N<sub>2</sub>O, as the second cleaning gas, is supplied at rates of about 0.05 to about 0.20 to the total flow of the first cleaning gas, wherein the total flow of the first cleaning gas is 160sccm, and the cleaning rate, the DRE and the MMTCE are measured at each flow rate.

[0046] The addition of  $N_2O$  to the first cleaning gas,  $C_4F_8/O_2$ , up to the rate of about 0.05, increases the cleaning rate, and the highest cleaning rate is about 300 nm/min at the rate of about 0.05. Further additions of  $N_2O$  do not particularly change the cleaning rates as compared with the cleaning rate at 0.05  $N_2O$ .

[0047] There are differences in the cleaning rates at the center of the substrate holder 16, at the side wall of the chamber 10, and at the front wall of the chamber 10, and the differences in the cleaning rates are less than about 10%, thereby showing uniform cleaning rates.

[0048] The DREs of  $C_4F_8$  with  $N_2O$  are higher than 99%, and thus it is understood that almost all of supplied  $C_4F_8$  is destructed during the cleaning process.

[0049] The PFC gases emitted during the cleaning process are measured for about 2 minutes, and the MMTCEs of the PFC gases decrease until the addition of  $N_2O$  to  $C_4F_8/O_2$  is 0.15. Therefore, the additions of  $N_2O$  to  $C_4F_8/O_2$  are effective in controlling the global warming effect.

[0050] Meanwhile, the MMTCEs of the PFC gases emitted while cleaning the silicon nitride of about 1,000 nm are calculated. When  $N_2O$  is not added to the first cleaning gas, the MMTCE is about  $1.3\times10^{-9}$ . When the flow rate of  $N_2O$  to the first cleaning gas is about 0.05, the MMTCE decrease by about 75% as compared with the MMTCE of the case without  $N_2O$ , and is about  $3.5\times10^{-10}$ . When the flow rate of  $N_2O$  to the first cleaning gas is about 0.2, the MMTCE is about  $5.0\times10^{-10}$ .

## [0051] Second embodiment

[0052] In a second embodiment, RF power of about 800Watts for generating plasma is applied to the remote plasma generator 70 of FIG. 1, and the pressure in the chamber 10 of

FIG. 1 is about 400mTorr. Other conditions of the second embodiment are the same as conditions of the first embodiment, and the same apparatus in the first embodiment may be used. In addition, samples for measuring cleaning rates of the chamber are located at the center of the substrate holder 16, at the side wall of the chamber 10, and at the front wall of the chamber 10, respectively.

[0053]  $C_4F_8O$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2O$  or NO is used as the second cleaning gas.  $C_4F_8O$  of about 40sccm and  $O_2$  of about 180sccm are supplied into the remote plasma generator 70. When the second cleaning gas is not supplied, the cleaning rate is about 118 nm/min, and the DRE and the MMTCE are about 96% and about  $7.023 \times 10^{-10}$ , respectively.

[0054]  $N_2O$  or NO, as the second cleaning gas, is supplied at rates of about 0.05 to about 0.25 to the total flow of the first cleaning gas, respectively, wherein the total flow of the first cleaning gas is 220sccm, and the cleaning rate, the DRE and the MMTCE are measured at each flow rate of each second cleaning gas.

[0055] In the case that the second cleaning gas is N<sub>2</sub>O, the additions of N<sub>2</sub>O to the first cleaning gas, C<sub>4</sub>F<sub>8</sub>O/O<sub>2</sub>, increase the cleaning rates, and the cleaning rate is about 1,190 nm/min at the flow rate of about 0.15. Further additions of N<sub>2</sub>O do not particularly change the cleaning rates as compared with the cleaning rate at 0.15 of N<sub>2</sub>O to the first cleaning gas. The differences in the cleaning rates at the three locations are about 13%. The DREs of C<sub>4</sub>F<sub>8</sub>O are higher than 96% without regard to additions of N<sub>2</sub>O. The MMTCE at the addition of 0.05 N<sub>2</sub>O to C<sub>4</sub>F<sub>8</sub>O/O<sub>2</sub> decreases by about 95%. Therefore, the additions of N<sub>2</sub>O to C<sub>4</sub>F<sub>8</sub>O/O<sub>2</sub> are effective in controlling the global warming effect.

[0056] When NO is added as the second cleaning gas to  $C_4F_8O/O_2$ , the cleaning rate increases, and is about 1,150 nm/min at the flow rate of 0.05 NO to  $C_4F_8O/O_2$ . Although NO is added over 0.05 of the flow rate, the cleaning rates are about the same value as the cleaning rate at 0.05 of NO to the first cleaning gas. The differences in the cleaning rates at the three locations are about 11%, and the cleaning is uniform at the three locations. The DREs of  $C_4F_8O$  are similar without regard to additions of NO. The MMTCE at the addition of 0.05 NO to  $C_4F_8O/O_2$  decreases by 93% as compared with the MMTCE when NO is not added.

#### [0057] Third embodiment

[0058] In a third embodiment, RF power for generating plasma is about 300Watts and the pressure in the chamber is about 400mTorr. The third embodiment may use a capacitively coupled plasma (CCP) system.

[0059] Silicon nitride (5 cm  $\times$  5 cm) formed on a silicon wafer is used as samples for measuring the cleaning rates of the chamber.  $C_4F_8O$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2$  is used as the second cleaning gas.  $C_4F_8O$  of about 16sccm and  $O_2$  of about 64sccm are supplied into the chamber. When the second cleaning gas is not supplied, the cleaning rate is about 507.7 nm/min, and the DRE and the MMTCE are about 98.38% and  $3.58\times10^{-9}$ , respectively.

[0060]  $N_2$  is supplied as the second cleaning gas at rates of about 0.05 to about 0.20 to the total flow of the first cleaning gas, respectively, wherein the total flow of the first cleaning gas is 80sccm, and the cleaning rate, the DRE and the MMTCE are measured at each flow rate.

[0061] The additions of  $N_2$  to the first cleaning gas,  $C_4F_8O/O_2$ , increase the cleaning rates, and the cleaning rate is highest at the flow rate of 0.10 of  $N_2$  to  $C_4F_8O/O_2$ . The cleaning

rate at 0.10 of  $N_2$  to  $C_4F_8O/O_2$  increases by about 32.5% as compared with the cleaning rate when  $N_2$  is not added. Although  $N_2$  is added over the flow rate of 0.10, the cleaning rates are about the same value as the cleaning rate at 0.10 of  $N_2$  to the first cleaning gas.

[0062] The DREs of  $C_4F_8O$  are higher than 97% while  $N_2$  is added at the flow rates of 0.05 to 0.20 to  $C_4F_8O/O_2$ . The MMTCE at the addition of 0.10 of  $N_2$  to  $C_4F_8O/O_2$  decreases by about 38.0% as compared with the MMTCE the cleaning gas without  $N_2$ .

# [0063] Fourth embodiment

[0064] FIG. 2 shows a schematic view of an apparatus for manufacturing a semiconductor device used in the cleaning method according to a fourth embodiment of the present invention.

[0065] In FIG. 2, an upper electrode 12 and a lower electrode 14 are disposed in a chamber 10. The upper electrode 12 is connected to a radio frequency (RF) power supply 20 and the lower electrode 14 is grounded. A gas inlet 30 is equipped at the chamber 10, and a substrate holder 16 is disposed in the chamber 10. An exhaust line 32 is connected to the chamber 10 to exhaust cleaning residues. The exhaust line 32 is also connected to a booster pump 34 and a dry pump 36, and a control valve 40 is located in the exhaust line 32. The pressure in the chamber 10 can be regulated by the control valve 40. Nitrogen gas (N<sub>2</sub>) is used as a purging gas of the dry pump 36, and a flow rate of N<sub>2</sub> is uniformly maintained during a cleaning process. A cleaning rate of the chamber 10 is measured by a step-profilermeter 50, and a Fourier transform Infrared (FT-IR) spectrometer 60 is equipped at one end of the exhaust line 32 to measure the MMTCE of the PFC gases released during the cleaning process. Samples for measuring the cleaning rates are located on the substrate holder.

[0066] The fourth embodiment of the present invention may use a capacitively coupled plasma (CCP) system for generating plasma. RF power of about 350Watts is supplied and the pressure in the chamber is about 500mTorr during the cleaning.

[0067]  $C_4F_8O$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2O$  or NO is used as the second cleaning gas.  $C_4F_8O$  of about 16sccm and  $O_2$  of about 64sccm are supplied into the chamber 10. When the second cleaning gas is not supplied, the cleaning rate is about 600 nm/min, and the DRE and the MMTCE are about 98% and about  $3.6\times10^{-10}$ , respectively.

[0068] N<sub>2</sub>O or NO, as the second cleaning gas, is supplied at rates of about 0.05 to about 0.25 to the total flow of the first cleaning gas, respectively, wherein the total flow of the first cleaning gas is 80sccm, and the cleaning rate, the DRE and the MMTCE are measured at each flow rate of each second cleaning gas.

[0069] The cleaning rates are increased as  $N_2O$  or NO are added to the first cleaning gas,  $C_4F_8O/O_2$ , and particularly at flow rates of 0.05 to 0.15 to the first cleaning gas. The cleaning rates at additions of NO are higher than those at additions of  $N_2O$ .

[0070] The DREs are within a range of about 95% to about 99% without regard to additions and kinds of the second cleaning gas. The additions of the second cleaning gas to  $C_4F_8O/O_2$  decrease the MMTCEs. The MMTCE normalized to 1,000 nm/min of the cleaning rate for silicon nitride is about  $5.66\times10^{-10}$  when the second cleaning rate is not added. The normalized MMTCEs decrease with the additions of the second cleaning gases to the first cleaning gas, and are about  $2.52\times10^{-10}$  at 0.15 of NO and  $3.31\times10^{-10}$  at 0.15 of  $N_2O_3$  respectively.

## [0071] Fifth embodiment

[0072]  $C_3F_8$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2$ , NO, or  $N_2O$  is used as the second cleaning gas.  $C_3F_8$  of about 150sccm and  $O_2$  of about 350sccm are supplied. When the second cleaning gas is not added, the cleaning rate is about 258.9 nm/min, and the DRE and the MMTCE are about 99% and about  $1.4 \times 10^{-10}$ , respectively.

[0073] In the case of  $N_2$ , the cleaning rate is highest at the addition of 0.10  $N_2$  to  $C_3F_8/O_2$ , and is about 304.3 nm/min. In the case of NO, the cleaning rate is highest at the addition of 0.05 NO to  $C_3F_8/O_2$ , and is about 433 nm/min. In the case of  $N_2O$ , the cleaning rate is highest at the addition of 0.10  $N_2O$  to  $C_3F_8/O_2$ , and is about 426.5 nm/min.

[0074] The DREs are about 99% without regard to additions and kinds of the second cleaning gas.

[0075] The additions of the second cleaning gases, N<sub>2</sub>, NO and N<sub>2</sub>O, to C<sub>3</sub>F<sub>8</sub>/O<sub>2</sub> decrease the MMTCEs. The MMTCEs are rapidly decreased when the flow rate of the second cleaning gas to the first cleaning gas is 0.05, and decreased by about 30% to about 40% as compared with the values when the second cleaning gases are not added.

## [0076] Sixth embodiment

[0077]  $C_4F_8$  is used as the fluorocarbon gas of the first cleaning gas, and  $N_2$ , NO, or  $N_2O$  is used as the second cleaning gas.  $C_4F_8$  of about 100sccm and  $O_2$  of about 400sccm are supplied. When the second cleaning gas is not added, the cleaning rate is about 232.9 nm/min, and the DRE and the MMTCE are about 99% and about  $6.15 \times 10^{-11}$ , respectively.

[0078] In the case of  $N_2$ , the cleaning rate is highest at the addition of 0.15  $N_2$  to  $C_4F_8/O_2$ , and is about 333.6 nm/min. In the case of NO, the cleaning rate is highest at the addition of 0.15 NO to  $C_4F_8/O_2$ , and is about 314.5 nm/min. In the case of  $N_2O$ , the cleaning rate is highest at the addition of 0.15  $N_2O$  to  $C_4F_8/O_2$ , and is about 307.5 nm/min.

[0079] The DREs are about 99% without regard to additions and kinds of the second cleaning gas.

[0080] The additions of the second cleaning gases,  $N_2$ , NO and  $N_2O$ , to  $C_4F_8/O_2$  decrease the MMTCEs. The MMTCEs are lowest when the second cleaning gas is added at the flow rate of 0.15 to the first cleaning gas, and decreased by about 25% to about 40% as compared with the values when the second cleaning gases are not added.

## [0081] Comparison

[0082] To compare the results from the embodiments of the present invention, another cleaning process using NF<sub>3</sub> as a cleaning gas is performed in the same conditions and the same apparatus as the first embodiment. At this time, argon gas (Ar) is added to NF<sub>3</sub>. The flow of NF<sub>3</sub> is about 20sccm and the flow rate of Ar mixed to NF<sub>3</sub> is varied.

[0083] The additions of Ar to NF<sub>3</sub> initially increase the cleaning rate, and the highest cleaning rate is about 310 nm/min at the flow rate of 0.5 Ar to NF<sub>3</sub>. Also, the differences in the cleaning rates among the three locations, that is, at the center of the substrate holder, at the side wall of the chamber, and at the front wall of the chamber, are less than 10 %, thereby showing uniform cleaning rates regardless of location.

[0084] The DREs are over 99% without regard to additions of Ar, thereby showing that most of fed NF<sub>3</sub> gas is destructed.

[0085] Also, the MMTCEs are about  $0.5 \times 10^{-10}$  without regard to additions of Ar. Meanwhile, the MMTCEs normalized to 1,000 nm/min of the cleaning rate for silicon nitride are within a range of about  $10.0 \times 10^{-10}$  to about  $12.5 \times 10^{-10}$ .

[0086] As mentioned above, the cleaning method of the present invention decreases global warming gases released after cleaning process, and thus reduces global warming effect.

[0087] The cleaning method of the present invention increases cleaning rates, thereby improving processing efficiency, and the chamber is uniformly cleaned by the cleaning method of the present invention.

[0088] In addition, since the cleaning gas used in the present invention is cheaper than NF<sub>3</sub>, the manufacturing costs of the semiconductor device are decreased.

[0089] It will be apparent to those skilled in the art that various modifications and variations can be made in the fabrication and application of the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.